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FINAL TECHNICAL REPORT

P49620-89-C-0073

"ULTRASTRUCTURE AND PROPERTIES OF RIGID ROD POLYMERS"

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RESEARCH OBJECTIVES AND RESULTS

The structure and properties of PBZT and PBO fibers and films depend critically in the detailed processing. Investigation of the coagulation process is of significant interest because this is where the initial solid state polymer structure forms and the starting point from which all other post treatment microstructures evolve. Research under F49620-89-C-0073 has concerned an analysis of crystal solvates in a PBZT/PPA/water system, a general geometrical classification scheme for grain boundaries in PBZO, the analysis of compressive strength of PBZT/PEEK film laminates after sol-gel microcomposite processing, a morphological study of kink bands in PBZT and PBZO fibers to determine the cause of the relative weakness of the fibers in compression, and a microstructural examination of PBZO fibers as a function of heat treatment processing.

Two crystal solvates, a co-crystal of polymer and solvent, were discovered in the PBZT/polyphosphoric acid (PPA)/ water system. The crystal solvates formed during mild coagulation of the nematic spinning solution. Transitions between the nematic solution and the crystal solvates of the solid PBZT crystal were studied by X-ray diffraction. Of particular interest was crystal solvent form I since this is a very highly three-dimensionally ordered structure suggested to arise from unique associations between protonated PBZT polycations and oligomeric PPA anions [1].

Sol-gel processing has been applied to rigid-rod fibers for the first time to form PBZT/SiO₂ microcomposites. The sol impregnates the microfibrillar network in the as-coagulated fiber and, upon curing to the glass, serves to inhibit microfibrillar buckling during compression [2].

The analysis of grain boundaries in extended-chain polymers is key to understanding physical properties since the crystallite size is rather small in PBZT and PBZO fibers and films while the crystallinity is nearly 100 %, indicating a very large grain boundary area per unit volume. As such, grain boundaries play a significant role in compressive deformation behavior in high strength fibers such as PBZT and PBZO and in dopant uptake and resultant electrical conductivity for rigid-rod materials such as polyparaphenylene vinylene. We classified grain boundaries in rigid-rod macromolecular crystals into four types; these types are, in order of increasing energy: lateral chain invariant, lateral chain rotation, axial chain invariant, and axial chain rotation. Experimental evidence for these different types of boundaries was obtained from high resolution electron microscopy (HREM) studies of the rigid-rod polymer

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PBZO. We also analyzed possible molecular mechanisms for grain boundary motion [3].

Wide angle X-ray scattering, electron diffraction and HREM were used to extensively characterize the fine scale structure of PBZO. The scattering patterns allowed indexing of the PBZO to a nonprimitive ($N = 2$) monoclinic space group Pc (No. 7). The crystallite size, shape and orientation were directly determined from HREM lattice images [4].

PBZT and PBZO fibers are weak in compression, with failure occurring by strain localization in well-defined kink bands. We studied the morphology PBZT and PBZO kink bands in detail in order to help elucidate the molecular mechanisms involved in this deformation process. We found that the typical dimensions of a kink in the direction of the fiber axis (~ 30 nm) is smaller than the length of the average PBZT or PBZO molecule (100nm). Also, the boundary between the kinked and unkinked regions is well defined. Low-dose, HREM of the kink interior revealed local, high angle changes in chain orientation, indicative of covalent bond bending or breaking. We also proposed practical methods for improving compressive strength based on these mechanistic insights [5].

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1. Y. Cohen, Y. Sarayama and E. L. Thomas, "Crystal Solvates in the Poly[*p*-phenylene(benzo[1,2-*d*:4,5-*d'*]bisthiazole-2,6-diyl)]/Poly(phosphoric acid)/Water System." *Macromolecules*, 24, 1161 (1991).
2. R. F. Kovar, R. W. Lusignea, R. R. Haghighat, C. Pantano, and E. L. Thomas, "High Compressive Strength Ordered Polymer Fibers and Films Via Sol Gel Microcomposite Processing." *Proceedings of the Materials Research Society* 175, 193 (1990).
3. D. C. Martin and E. L. Thomas, "Grain Boundaries in Extended-Chain Polymers: Theory and Experiment." *Philosophical Magazine*, accepted November, 1990.
4. D. C. Martin and E. L. Thomas, "Ultrastructure of Poly(*p*-phenylenebenzo bisoxazole) Fibers." *Macromolecules*, in press.
5. D. C. Martin and E. L. Thomas, "Micromechanisms of Kinking in Rigid-Rod Polymer Fibers." *J. Materials Science*, in press.

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Crystal Solvates in the Poly[*p*-phenylene(benzo[1,2-*d*:4,5-*d'*]bisthiazole-2,6-diyl)]/ Poly(phosphoric acid)/Water System

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ABSTRACT: Two types of crystal solvates, formed by cocrystallization of the polymer and its solvent, were found in the poly[*p*-phenylene(benzo[1,2-*d*:4,5-*d'*]bisthiazole-2,6-diyl)]/poly(phosphoric acid)/water (PBZT/PPA/water) system. These crystal solvates are formed during moderate coagulation of the liquid crystal phase of the PBZT/PPA system. Structural transitions between the nematic phase, the crystal solvates, and the PBZT crystal were studied by X-ray diffraction. The structural changes are associated with the absorption or removal of water. The different crystalline phases differ in their unit cell dimensions and in the extent of three-dimensional order in the packing of the parallel chains. The sequence of phases encountered upon increased water absorption is as follows: the liquid crystal phase; an ordered crystal solvate (form I); a less ordered crystal solvate (form II); and the poorly ordered crystalline PBZT phase. The well-developed crystalline order in the form I crystal solvate is considered to reflect unique associations between the protonated PBZT polycations and the oligomeric PPA anions. A schematic phase diagram is suggested for the ternary system composed of a rodlike polymer, a protonating solvent, and a deprotonating nonsolvent, which is in qualitative agreement with the observed phase transitions.

Introduction

Poly[*p*-phenylene(benzo[1,2-*d*:4,5-*d'*]bisthiazole-2,6-diyl)] (PBZT) is a rigid rodlike polymer from which fibers and films exhibiting high tensile modulus and strength are fabricated.^{1,2} In the processing of PBZT fibers and films, an oriented nematic solution of PBZT in a strong acid is coagulated by a nonsolvent. Most commonly, the solvent is poly(phosphoric acid) (PPA), which is the polymerization medium for PBZT,³ and water is used as the coagulant. Studies of the morphology,^{4,5} and mechanical properties,⁶ which develop during coagulation of the PBZT/PPA solution in the process of fiber spinning have shown the formation of a network of microfibrils, the width of which is <100 Å. The microfibrillar network has the ability to sustain a tensile force that is comparable to that of the subsequently dried fiber. These studies indicate that the basic structural features responsible for the mechanical properties are set during coagulation and suggest that improved mechanical properties may be obtained by control of the coagulation process.

The structure of the crystalline PBZT phase, which is formed by coagulation in water, and subsequent improvements in crystalline order and orientation by postprocessing heat treatment under tension have been studied extensively.⁷⁻¹¹ However, details of the structural transitions during coagulation have not been studied. Such transitions may be revealed by coagulation under mild conditions. In solutions of PBZT in methanesulfonic acid (MSA), a crystal solvate phase can be formed by mild coagulation with moist air.^{12,13} Crystal solvate phases, which result from cocrystallization of the polymer with its solvent, have been observed to form in solutions of several

rigid polymers.^{14,15} An understanding of the formation of crystal solvates in solutions of rigid polymer may be important in optimizing the coagulation process and the resultant mechanical properties.¹⁶

In a previous study on the coagulation of the PBZT/PPA system under mild conditions by 85% phosphoric acid, a crystal solvate phase has been observed.¹⁷ However, we recently found that two forms of crystal solvates can be formed in the PBZT/PPA/coagulant system, the coagulant being either water or phosphoric acid. In this paper we report on the conditions of phase transitions among the various phases: the nematic phase, the crystal solvates, and the PBZT crystal. We also report on the structure of the crystal solvates.

Experimental Section

The starting material is a uniaxially oriented nematic solution of PBZT in PPA. The PBZT solution, obtained from the Stanford Research Institute, had the following characteristics: PBZT concentration, 13.7% (by weight); P₂O₅ content of PPA, 82.6%; PBZT intrinsic viscosity (in MSA), 25 dL/g, which indicates a molecular weight of approximately 40 000.¹⁸ The PBZT/PPA solution was oriented by extrusion through a tubular die (2-mm gap, extrusion temperature 120 °C) at Foster Miller Inc. Subsequently, samples were handled under dry nitrogen. Coagulated samples were obtained from the oriented solution by immersion either in water or in commercial (85%) phosphoric acid. Structural transitions due to absorption of a small amount of moisture were induced by exposing the oriented solution to atmospheric moisture for a few minutes.

The structure of the samples was investigated by X-ray diffraction using monochromatized Cu Kα radiation with a Statton camera or a cylindrical camera. To avoid structural changes during the X-ray diffraction experiment, the samples were sealed

HIGH COMPRESSIVE STRENGTH ORDERED POLYMER FIBERS AND FILMS
VIA SOL GEL MICROCOMPOSITE PROCESSING

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ABSTRACT

Sol-gel glass microcomposite processing of polybenzobisthiazole (PBZT) films increased the compressive strength of PBZT/PEEK film laminates by more than four times. The presence of glass within microfibrillar regions of PBZT/sol-gel glass microcomposite films inhibited microbuckling during compression and greatly increased resistance to compressive failure.

Studies of PBZT/sol-gel glass microcomposite film morphology conducted at UMass by E.L. Thomas and at Penn State by C. Pantano indicated sol-gel glass precursor solutions had condensed within PBZT to produce a fine-scale (100 to 300Å) granular structure, homogeneously distributed throughout PBZT lamellae of microfibrils.

In a parallel effort, we have successfully extended sol-gel microcomposite processing technology for the improvement of compressive strength in ordered polymer fibers. Details concerning our results will be discussed.

INTRODUCTION

The purpose of this Small Business Innovative Research (SBIR) program was to develop a new class of microcomposite materials that would exhibit the high tensile strength and toughness of ordered polymers and the excellent compressive strength of glass. During Phase I, we demonstrated the feasibility of improving PBZT ordered polymer film compressive properties by infiltration with sol-gel glass reagents. The Phase II program addressed the following: analysis of PBZT/sol-gel glass morphology, development of sol-gel reagent infiltration processes, lamination of PBZT/sol-gel films and microcomposite of prototype parts to demonstrate improved compressive strength performance over other materials.

GRAIN BOUNDARIES IN EXTENDED-CHAIN POLYMERS:
THEORY AND EXPERIMENT

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Abstract

A general geometrical classification scheme for grain boundaries in extended-chain polymers is presented. The analysis is an extension of a scheme originally presented by Bevis to describe deformation twins in polymers. Bevis recognized the importance of the orientation of the covalently bonded chain backbone within the crystallite, and referred to boundaries as "chain invariant" or "chain rotation" depending on whether chains in adjacent domains were parallel or not. We consider an important additional parameter: the orientation of the grain boundary plane. We classify those grain boundaries which are parallel to the two chain directions as "lateral", and those which are not "axial". These two parameters lead directly to four types of grain boundaries which are, in order of increasing energy: lateral chain invariant, lateral chain rotation, axial chain invariant, and axial chain rotation. Experimental evidence for these different types of boundaries are presented from High Resolution Electron Microscopy (HREM) studies of the rigid-rod polymer poly(paraphenylene benzobisoxazole) (PBZO or PBO). Possible molecular mechanisms for grain boundary motion are also discussed.

Ultrastructure of Poly(*p*-phenylenebenzobisoxazole) Fibers

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ABSTRACT: The ultrastructure of poly(*p*-phenylenebenzobisoxazole) (PBZO or PBO) was studied as a function of processing condition by wide-angle X-ray scattering (WAXS), selected-area electron diffraction (SAED), dark-field transmission electron microscopy (DF), and high-resolution electron microscopy (HREM). The development of single-crystal texturing in thin films made it possible to index the PBZO scattering patterns to a nonprimitive ($N = 2$) monoclinic space group Pc (No. 7). The new unit cell parameters are $a = 1.120$ nm, $b = 0.354$ nm, $c = 1.205$ nm, $\gamma = 101.3^\circ$, and $\rho_{x1} = 1.66$ g/cm³, with neighboring chains in the a direction placed at relative axial translations of $\pm 1/4c$. HREM images of the 0.55- (200) and 0.35-nm (010) lateral spacings between PBZO molecules enabled the crystallite size, shape, and relative orientations to be directly determined. Defects within and between PBZO crystallites were observed, and molecular models are presented that are consistent with these observations.

A. Introduction

The rigid-rod polymers poly(*p*-phenylenebenzobisthiazole) (PBZT) and poly(*p*-phenylenebenzobisoxazole) (PBZO or PBO) are of considerable interest for high-performance applications. The chemical structures of PBZT and PBZO are shown in Figure 1. Historically, more effort has been expended in refining the spinning and processing steps for PBZT fiber because it was originally easier to obtain higher molecular weight PBZT than PBZO. However, recent advances in synthetic techniques have made it possible to reproducibly obtain high molecular weight PBZO¹ and PBZO is now under commercial development by Dow Chemical Co. It is therefore reasonable to expect an expanded interest in the relationship between structure and properties of PBZO fiber.

We investigate the ultrastructure of *cis*-PBZO fiber by wide-angle X-ray scattering (WAXS), selected-area electron diffraction (SAED), dark-field transmission electron microscopy (DF), and high-resolution electron microscopy (HREM). The morphology was examined as a function of postspinning heat treatment of the PBZO fiber.

Our interest concerns the molecular ordering that occurs in as-spun PBZO fiber and its evolution during tensioned heat treatment. Information about the size, shape, orientation, and internal perfection of PBZO crystallites is important for a full understanding of the unique mechanical properties of these materials. In particular, the tensile moduli of the best PBZO fibers (320 GPa) are now approaching values expected theoretically (730 GPa) from semiempirical AM1 molecular orbital calculations of isolated molecules.² The extremely high tensile moduli and strengths of rigid-rod polymer fibers suggests that understanding and possibly controlling morphological defects (such as the dislocations within and grain boundaries between crystalline domains) may be critical for further optimizing properties.

B. Background

The structure of PBZO fiber was first studied by WAXS by Worsham and Kim.³ The WAXS pattern of the as-

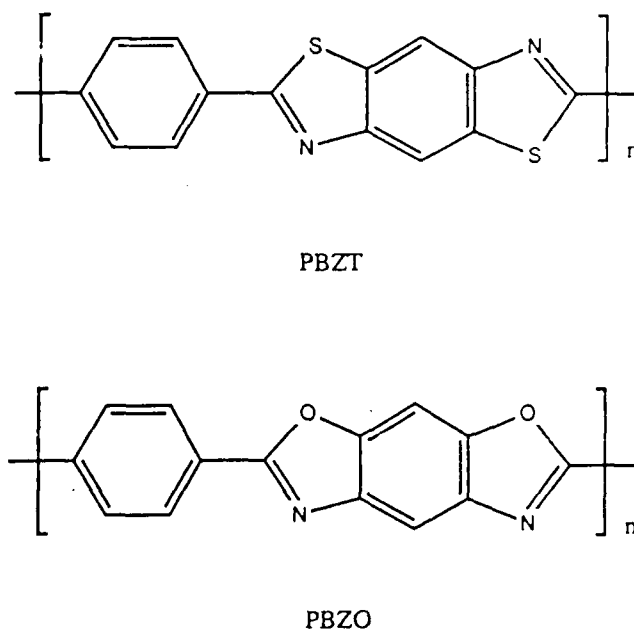


Figure 1. Chemical structures of *trans*-PBZT and *cis*-PBZO.

spun fiber showed good orientation, with two strong equatorial reflections at spacings of 0.555 and 0.335 nm and weak scattering on the first and third layer lines (1.135 nm) along the fiber direction.

Model calculations by Bhaumik et al.⁴ using an empirical molecular orbital approach for the interactions between *cis*-PBZO molecules showed that there is a minimum in the energetic interactions between neighboring PBZO monomers at a characteristic axial shift of 0.2 nm for molecules packed side by side (0.62 nm apart) and at 0.3 nm for molecules packed face to face (0.35 nm apart).⁴ However, the energy troughs as a function of relative axial position were shallow (3 kcal/mol; 5 kT), so it might be expected that PBZO molecules would exhibit axial disorder in the solid state as does PBZT.⁵

The study of Bhaumik et al.⁴ did not investigate the effect of different internal conformations of the *cis*-PBZO molecule. The energetics of the interactions between neighboring PBZO molecules might be quite sensitive to internal rotations of the heterocyclic group about the chain axis. For *cis*-PBZO, the interactions between neighboring molecules may be particularly sensitive to such internal

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Micromechanisms of kinking in rigid-rod polymer fibres

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The tensile strengths of fibres of the rigid-rod polymers poly(paraphenylene benzobisthiazole) (PBZT) and poly(paraphenylene benzobisoxazole) (PBZO) are excellent, and therefore are of particular interest for high-performance structural applications. However, these fibres are a factor of ten weaker in compression, with failure occurring by strain localization in well-defined kink bands. Here, we study the morphology of PBZT and PBZO kink bands in detail, in order to help elucidate the molecular mechanisms involved in this deformation process. We found that the typical dimensions of a kink in the direction of the fibre axis (~ 30 nm) were smaller than the length of an average PBZT or PBZO molecule (100 nm). Also, the boundary between the kinked and unkinked regions was well-defined. Low-dose, high-resolution electron microscopy (HREM) of the kink interior revealed local, high-angle changes in chain orientation, indicative of covalent bond bending or breaking. The kink boundaries exhibit "sharp" or "smooth" features which seem to be related to the local tensile or compressive nature of the stress field. A model for kink nucleation and propagation in terms of ~~edge~~ ^{partial} dislocations is presented and discussed. A stress analysis using this model has been developed, and comparison with experimental data suggests that kinks tend to propagate towards regions of higher compressive stress. This observation is interpreted in terms of dislocation pinning (in areas of hydrostatic tension) and the nucleation of dislocation pairs (in areas of hydrostatic compression) due to the asymmetric nature of the intermolecular energy potential. Finally, practical methods for improving compressive strength based on these mechanistic insights are proposed.

1. Introduction

The tensile moduli and strengths of rigid-rod polymer fibres poly(paraphenylene benzobisthiazole) (PBZT) and poly(paraphenylene benzobisoxazole) (PBZO) are excellent. Theoretical predictions of PBZT and PBZO modulus have been obtained using semi-empirical quantum mechanical (minimum neglect of differential overlap) methods [1, 2]. The theoretically predicted moduli of *trans*-PBZT and *cis*-PBZO are 605 and 730 GPa, respectively [2]. Values nearly 50% of this theoretically predicted modulus have now been obtained experimentally [3]. Tensile strengths up to 4.9 GPa for PBZO and 4.2 GPa for PBZT have been observed [3, 4]. However, both PBZO and PBZT fibres are about a factor of ten weaker in compression, with failure occurring by strain localization into kink bands.

The compressive strength problem has become a severe limitation for the application of rigid-rod polymers in structural components. Hence, a deeper understanding of the molecular motions involved in

kinking is a critical concern for future success in the design and processing of high-strength, high-modulus polymer fibres.

This paper presents a study of the morphology of kink bands in rigid-rod polymer fibres using optical microscopy (OM), dark-field (DF) and bright-field (BF) transmission electron microscopy, selected-area electron diffraction (SAED), and high-resolution electron microscopy (HREM). Elsewhere we investigate the thermodynamics of kinking by quantitative measurements of kinking in fibres during known amounts of compressive plastic deformation [5]. We discuss a model for kinking which involves the nucleation and growth of a kink across a fibre and describe the molecular motions involved in this deformation process. The kink band is envisioned to be a region of shear deformation separated from the undeformed part of the sample by high-angle axial chain rotation grain boundaries and partial edge dislocations. The information and insight about the molecular mechanisms and energetics of kinking obtained by this

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